

An Electrical Method for the
Simultaneous Determination
of Hydrogen, Carbon and
Sulphur in Organic
Compounds.

DISSERTATION

SUBMITTED TO THE BOARD OF UNIVERSITY STUDIES OF
THE JOHNS HOPKINS UNIVERSITY IN CONFORMITY
WITH THE REQUIREMENTS FOR THE DEGREE
OF DOCTOR OF PHILOSOPHY.

BY

C. WALTER GRAY.

1906.

EASTON, PA. :
ESCHENBACH PRINTING COMPANY

An Electrical Method for the Simultaneous Determination of Hydrogen, Carbon and Sulphur in Organic Compounds.

DISSERTATION

SUBMITTED TO THE BOARD OF UNIVERSITY STUDIES OF
THE JOHNS HOPKINS UNIVERSITY IN CONFORMITY
WITH THE REQUIREMENTS FOR THE DEGREE
OF DOCTOR OF PHILOSOPHY.

BY



C. WALTER GRAY.

1906.

EASTON, PA. :
ESCHENBACH PRINTING COMPANY



Digitized by the Internet Archive
in 2026

CONTENTS.

Acknowledgment	4
I. Historical	5
II. The Electrical Method	5
Apparatus Required	5
The Platinum Coil	6
The Platinum Disc	8
The Platinum Boat	8
The Electric Stove	9
The Calibration of the Electric Stove	10
Peroxide of Lead	11
The Procedure during an Analysis	12
The Protection of the Combustion Tube	13
Calculation of Results	16
III. Combustion of Compounds Containing Carbon, Hydrogen, Sulphur and Oxygen	16
Analyses of "Sulphonal"	16
IV. Combustion of Compounds Containing Nitrogen	17
Analyses of Phenylthiourea	17
Analyses of Phenylthiosemicarbazide	17
Analyses of Acetylphenylthiosemicarbazide	17
Analyses of Diphenylthiourea	17
Analyses of Parasulphaminebenzoic Acid	18
Analyses of Phenylthiomethylethoxyurazole	18
Analyses of Thiourea	18
V. Combustion of Commercial Compounds	18
VI. Determination of the Halogens	19
VII. Biographical Sketch	20

ACKNOWLEDGMENT.

The author desires to express his deep gratitude to President Remsen for the instruction and inspiration which have been afforded by his lectures. To Professor Jones his thanks are also due for instruction in the lecture room and in the laboratory.

This investigation was undertaken and carried out under the direction of Professor Morse. To him the author desires to express special thanks for his valuable suggestions, which have contributed essentially to the success of the work.

AN ELECTRICAL METHOD FOR THE SIMULTANEOUS DETERMINATION OF HYDROGEN, CARBON AND SULPHUR IN ORGANIC COMPOUNDS.

The catalytic effect of hot platinum was used as early as 1876 by Kopfer¹ as a substitute for copper oxide in the combustion of organic compounds. The large amount of platinum, however, required by this method made its general introduction prohibitive.

Later, Dennstedt² devised a method for the combustion of organic compounds by means of platinized quartz. The amount of platinum required by this method is small, but the results obtained are not always reliable.

The use of peroxide of lead, as an absorbent for the oxides of sulphur and of the oxides of nitrogen in the combustion of organic compounds, is first mentioned by Warren,³ in 1864. It has been used by numerous experimenters since that time.

In 1904 Morse and Taylor⁴ described the first method for the combustion of organic compounds, based upon the use of electrically heated platinum as a source of the energy employed to effect the combustion. Not only is the heating effect of the electric current utilized, but also of the catalytic effect of the hot platinum. The advantages of the method as given by them, and which have been substantiated by experience, are as follows: (1) "The apparatus required is so compact and of such small dimensions that the combustion can be made at the working table of the student; (2) the waste of energy is much smaller than in the older methods; (3) the time consumed in preparing for and making a combustion is considerably diminished; (4) much greater ease in regulating the combustion is possible."

The apparatus, Figs. 1 and 2, used in this investigation is identical with that described by Morse and Taylor,⁵ excepting

¹ J. Chem. Soc. (London) **29**, 660.

² Z. anal. Chem. **41**, 552.

³ *Ibid.*, **3**, 272 (1864).

⁴ Am. Chem. Jour. **33**, 591.

⁵ *Ibid.*, **33**, 591.

in so far as modifications were made necessary for the purpose of determining sulphur, at the same time with carbon and hydrogen. It consists of a thin, hard glass tube open at both ends and having a length of 650 mm. and an internal diameter of about 20 mm. One end is closed with a rubber stopper through which pass (1) a small porcelain tube E, having a length of 300 mm. and an external diameter of 6 mm. and (2) the exit tube L. The T-tube, D, is slipped over the end of the porcelain tube and is fastened to the latter by means of a short piece of rubber tubing, which is firmly tied in position by means of shoemaker's waxed thread. The horizontal end of D is closed by means of a stopper through which passes a platinum wire. The wire extends through the whole length of the porcelain tube and returns upon the outside in a series of suspended loops, and then passes through the rubber stopper as shown in Fig. 1. The ends of the wire are much thicker than the intermediate portion, in order to avoid the danger of overheating the stopper. The wire is prepared by heating to bright red heat 6 feet of No. 29 B. & S. gauge platinum wire, by passing an electric current through it, at the same time stretching the wire slightly. This operation serves to straighten the wire and remove some of the temper, and facilitates the winding. It is then wound upon a screw thread of such diameter that the resulting coil will be of about 14 mm. in diameter and, if the tension is kept constant during the winding, a uniform coil will result. It is removed from the screw by simply turning the thread while one end of the coil is held in the hand. If any inequalities in the size of the coils result from carelessness at this point, it may often be corrected by placing the coil, as it comes from the threads upon which it was formed, upon a glass tube or rod of the proper diameter, and drawing the coil down tightly to the surface of the rod. In this way the necessity of rewinding the coil is avoided. The coil is then ready to be placed upon the porcelain tube. One end of the coil is connected with a larger platinum wire (about 80 mm. of No. 18 B. & S. gauge) which passes through the T-tube D. This is then passed through the porcelain tube until about 22 mm. of the wire extend beyond D. Another piece of No.

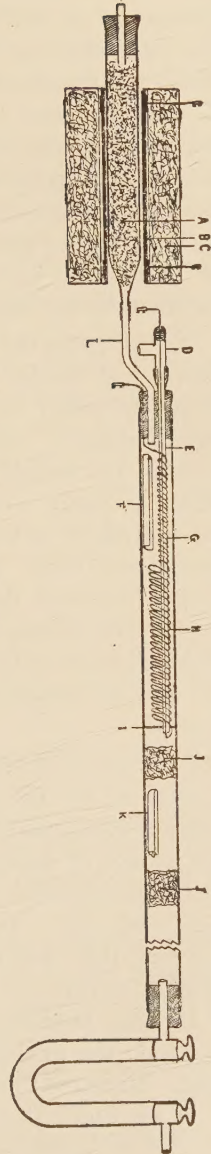


FIG. I.

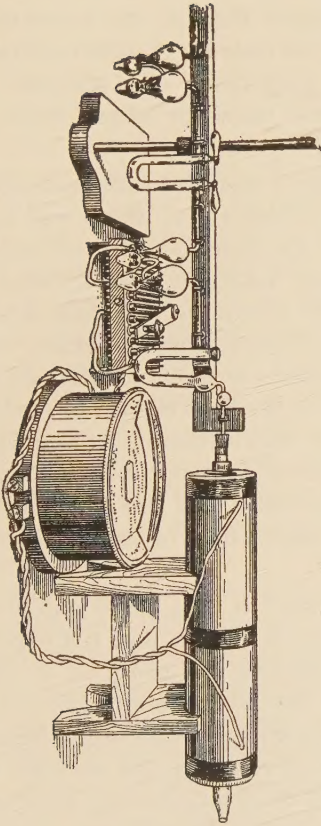


FIG. II.

18 B. & S. gauge platinum wire of about the same length is sharpened at one end and forced through the rubber stopper; the end which is within the combustion tube is given a few turns tightly about the porcelain tube, as shown in Fig. 1. It is then fastened to the coil which is connected with the source of current through the large terminal wires. The rear end of the porcelain tube passes through an eccentrically perforated platinum disk I, and the coils are thereby maintained in their proper position in the glass tube. The platinum disc is perforated by numerous fine openings which allow the products of the combustion to pass through.

To this point the new apparatus is identical with that used by Morse and Taylor.¹ The first modification, which was introduced to adapt the method to the determination of sulphur, simultaneously with carbon and hydrogen, was to wind the coils in the vicinity of G tightly about the porcelain tube, in order to make room for the platinum boat F, which, when an analysis is to be made, contains a weighed quantity of pure peroxide of lead. The rear end of the boat is open to facilitate contact between the products of combustion and the oxide of lead. The second change was to remove the rolls of oxidized copper gauze which formerly preceded and followed the boat K, and to substitute in their place plugs of asbestos fibre J and J'.

In an article published by Warren,² in 1864, there is described a method for the determination of carbon and hydrogen in organic compounds containing sulphur and nitrogen, in which the oxides of sulphur and also the oxides of nitrogen are absorbed in peroxide of lead maintained at a temperature between 150° and 200°. The author, however, does not mention any attempt that was made by him to determine the amount of sulphur or nitrogen absorbed by the use of peroxide of lead.

In 1892 Dennstedt³ described a method of organic analysis in which the oxides of nitrogen were absorbed by peroxide of lead. In order to maintain the peroxide of lead at the proper

¹ Am. Chem. Jour. **33**, 591.

² Z. anal. Chem. **3**, 272 (1864).

³ *Ibid.*, **41**, 532.

temperature for the absorption of the oxides of nitrogen, Bunsen burners, placed appropriately beneath, were used. This, clearly, was an unsatisfactory method of maintaining a condition of constant temperature to within a very limited range.

The apparatus A, B, C, which is placed in front of the combustion tube, is one designed to complete the absorption of the oxides of nitrogen, a portion of which is also retained in the peroxide of lead in F. It consists of a graphited porcelain tube B, which has a length of about 350 mm., the asbestos covering C and a glass tube A which is filled with asbestos fibre covered with peroxide of lead. This apparatus is, of course, omitted if the substance to be analyzed does not contain nitrogen. The tube A is connected on one end with the combustion tube by means of small glass tube L, and on the other end with the absorption train which is made up of a Marchand tube filled with granular calcium chloride, a Geissler bulb containing a concentrated potassium hydroxide solution, and a U-tube in which there is placed soda lime and calcium chloride. Beyond this is a U-tube of calcium chloride which serves as a guard tube to the soda lime. A dilute solution of palladium chloride, contained in a Geissler bulb, is placed at the end of the train. This solution is darkened at once by any incompletely burned material.

The clamps at the ends of the combustion tube serve only as supports and should not grip the tube so tightly, as to prevent free movement back and forth. Otherwise, the tube may be fractured, due to an unnecessary strain in consequence of an expansion and contraction to which it is subjected during the process of heating and cooling.

The method of graphiting porcelain tubes, like B and other objects for the purpose of electrical heating, has been fully described by Morse and Frazer¹ and the procedure need not, therefore, be explained in this connection.

When the stove has been painted sufficiently to carry about 0.35 ampere at 110 volts, and has been tested as to its uniformity of conductivity, it is placed in the asbestos coating C

¹ Am. Chem. Jour. **31**, 93.

and the temperature is allowed to rise to 300° , when the process of the "sweating" of the graphite coating is complete. After the stove has been treated in this manner the resistance of its coating remains constant for any given temperature below 300° .

To prepare the tube A., asbestos fiber is covered by sifting and mixing with as much peroxide of lead, which has previously been heated to 300° , *i. e.*, to the temperature necessary for the complete dehydration, as can be made to adhere to it and after filling the tube, care being taken to pack it loosely, an additional quantity of the peroxide is sifted in among the asbestos fibres. A single filling of the tube often suffices for as many as twenty analyses. During a combustion it is necessary to maintain the tube A at a temperature of about 175° , in order to insure the complete absorption of oxides of nitrogen. The apparatus must, therefore, be subjected to a species of calibration before it is used. To this end a current of dried air, approximately equal to that which normally flows through an apparatus during a combustion, is passed through A. A thermometer is inserted and the amount of current necessary to maintain a series of temperatures, *i. e.*, 150° , 175° , 200° , etc., is ascertained. It is of advantage to determine the amount of current required to maintain the stove at a series of temperatures over a wide range, since a stove of this type is of great value in numerous operations, such as the heating of Carius tubes, which often require long-continued heating at a constant temperature. Furthermore, the length of time required for a given current to bring the contents of the tube to a constant temperature is determined. It was found that, in a stove constructed as above described, a temperature of 150° was maintained by a current of 0.625 ampere at 35 volts, 175° by 0.725 ampere at 39.5 volts, and 200° by 0.825 ampere at 44 volts.

Approximately ten minutes were necessary to raise the stove to the required constant temperature. A calibration of this kind is not precise, since the rate of the flow of gas during a combustion is irregular and at all times of somewhat uncertain magnitude, but it is sufficiently accurate for all practical purposes.

Since the purity of the peroxide of lead, used for the absorption of the oxides of sulphur, in the platinum boat F, is of fundamental importance, too great care cannot be exercised in its preparation and subsequent purification before it is used in the analysis. The commercial peroxide of lead often contains a large percentage of impurities and, therefore, it has been found to be more satisfactory to prepare the peroxide in the laboratory. The method of preparation consists in treating about 1500 grams of the purest lead acetate with 3500 cc. of distilled water. The solution may then be filtered. To the filtrate is added 3500 cc. of a 20 per cent. solution of sodium hydroxide. Into this mixture is conducted purified chlorine gas, until a precipitate of the peroxide of lead is no longer formed. On account of the very fine state of division of the peroxide at this stage, it is of advantage to decant it repeatedly with water and not to attempt the filtration of the peroxide from the liquid in which it is suspended. It is then warmed with about 1200 cc. of dilute nitric acid, after which it is repeatedly decanted with distilled water. The small amount of lead sulphate and lead chloride, which the peroxide is certain to contain after being made as above described, is removed by the method of Dennstedt,¹ which consists in a long-continued agitation of the peroxide with a 4 per cent. solution of pure sodium carbonate. It is then thoroughly washed with water and is next treated with dilute nitric acid, after which it is repeatedly washed with water and dried, first at the temperature of the water-bath and finally at 300°, in order to insure complete dehydration. The quantity of lead oxide, PbO, which a unit weight of the peroxide of lead will yield, is determined with care, once for all, by heating to a temperature above 350°, weighed quantities of the peroxide to constant weight in a current of nitrogen, and the result is employed in finding the amount of sulphur trioxide produced in the combustion.

It is necessary, of course, that the peroxide, when weighed, shall be entirely free from moisture; it is therefore, prepared in the following manner: The boat F, after introducing the

¹ Z. anal. Chemie, 41, 535.

requisite amount of the peroxide—about 5 grams—is placed in a horizontal position in a glass weighing tube, having a ground glass stopper; the material, boat and the tube are then heated for half an hour at a temperature of 120° , and afterwards cooled in a desiccator. When the desiccator is opened for the purpose of weighing, the tube is immediately closed with the stopper.

The procedure, when an analysis is to be made, is as follows: The boat containing the weighed quantity of peroxide is inserted at F and that containing the substance to be burned at K. The two circuits, into which ammeters have been inserted—that through the combustion apparatus and also that through A B C, *i. e.*, in case the substance to be analyzed contains nitrogen, otherwise A B C is omitted—are closed through regulating rheostats, and dry air is passed through the whole apparatus, except of course the absorption train. The current through A B C is allowed to rise quickly to the quantity which is known to produce in A the most effective temperature for the absorption of the oxides of nitrogen, about 175° , while the current through the combustion apparatus is regulated more cautiously, *i. e.*, by raising the current by 0.2 ampere every two or three minutes until a current of 3.6 amperes flows through the coil. Care must be exercised to avoid heating the substance in K to a temperature at which it becomes volatile, before the apparatus has been dried out completely. This having been done, the absorption train is joined to A by means of a single perforated rubber stopper; the current of air which has been dried and purified by passing through silver sulphate solution, then over soda lime and, finally, over calcium chloride, entering at the rear is continued; oxygen, purified in the same manner, is admitted at D and the substance in K and the plug of asbestos J, in front of the boat, is heated by a lamp held in the hand. Experience has shown that a small flame, which is just sufficient to raise the temperature of the substance in the boat K to that point at which it has an appreciable vapor tension, is sufficient to complete the combustion. After the substance has been volatilized in this manner, if there remains in the boat K any unburned material, the current of air,

entering from behind, is replaced by one of oxygen and a larger flame is applied to the combustion tube in the vicinity of K. Thus the charred residue is rapidly burned and there is no difficulty in completing the actual combustion of a compound in twenty to thirty minutes. When the combustion of the substance has been finished, the current of oxygen, entering from behind, is replaced by one of dried and purified air, which is continued for some time in order to remove entirely the products of the combustion from the tube. The flow of the oxygen and of the air and the heating of the substance with the lamp, likewise the temperature of the platinum coils—all of which will depend somewhat upon the nature of the compound to be burned—are regulated according to the best judgment of the operator. If the substance is so volatile, that an explosion is likely to occur between the platinum disk and the asbestos plug, the air, admitted at the rear, is deprived of its oxygen by inserting a roll of copper wire gauze behind the last asbestos plug, and heating it with a lamp appropriately placed beneath the tube, or nitrogen, instead of air, is passed in from a gasometer. The latter method is preferable since, when the air is deprived of its oxygen by means of the copper wire gauze, the nitrogen, which passes on, is at a high temperature and there is a possibility of distilling the compound too rapidly, which results in a miscalculation as to the flow of oxygen necessary to burn the substance and which will be immediately shown by a blackening of the palladium chloride solution at the end of the absorption train.

By the passage of a current of 3.6 amperes through the coil, the larger loops of the coil are maintained at a moderately red heat and this insures, in the vicinity of the coil, a temperature which is amply sufficient for the combustion of the vapors of the substance to be analyzed. This also insures a temperature of between 330° and 340° , which is most advantageous for the absorption of the oxides of sulphur, in the peroxide of lead, under the small coils at G. This was determined by placing the bulb of a thermometer at G, while the maximum current of 3.6 amperes was flowing through the apparatus.

Considerable difficulty was formerly experienced by the

cracking of the combustion tube, especially during the cooling down period. This was caused by an improper selection of the glass used in the combustion tubing and, in addition, to a lack of precaution used to insure a thorough annealing of the tube after each combustion. It has been found by experiments, conducted with various kinds of glass, that the best results are to be obtained by the use of hard glass tubes of the Jena variety, the walls of which are approximately 1 mm. in diameter. If a tube is used whose walls are appreciably thicker than that above mentioned, there is a liability that it will crack, unless heated very slowly, due to a strain brought to bear upon the tube through excessive heating in certain points. The reverse of this is also true during the cooling down stage in the manipulation of the combustion.

Since the introduction of the use of properly selected combustion tubes, the walls of which are as thin as possible consistent with safety, the difficulties above-mentioned are, to a large degree, avoided; there are, however, several precautions which should be observed in order to avoid the cracking of the combustion tube. In heating the tube, preparatory to making a combustion, the management of the current has already been mentioned. In order to protect the portion of the tube in which the coils are contained, it is supported in that region in a semicircular trough of asbestos board, which is inserted in the clamp, between the lower jaw and the glass, and which supports the end of the tube, while the other end of the trough rests upon a support of sheet iron, notched at the top, and fastened to a block of wood on the laboratory table. The upper portion of the tube is protected, in the same region, by a semicircular trough of mica inverted over it and which rests upon the trough of asbestos below. In order to make the mica retain its curved form, there are fastened to its edges strips of metal, which, when bent into the required shape, preserve the curvature of the mica.

The gradual cooling of the combustion tube after each analysis must be accomplished with even greater care than the first heating. In order to insure an annealing of the glass, it has been found advantageous to deposit soot from a smoky

flame upon the exposed portions of the tube, and when this has been properly accomplished there is very little liability to fracture when the tube is reheated.

In order to protect more completely the combustion tube while hot, and also while cooling, from drafts of cold air which are liable to cause the tube to crack, there is placed in a vertical position behind, and about 50 mm. distant from the tube, an asbestos board of about 650 mm. in length and which extends from the combustion table to some distance above the apparatus. At each end of the tube may be placed pieces of asbestos board at right angles to the larger board behind and of the same height, and through which the tube extends a few millimeters at each end. In addition to the above precautions there may be clamped an iron rod, parallel to the tube and a few millimeters above it, over which is hung an inverted semicircular trough of asbestos board. The above-described protections not only serve to prevent the drafts of cold air striking the tube, but they also assist in the thorough annealing of the tube after each combustion, by preventing the tube from cooling too rapidly. Another precaution which should be observed is to prevent the red hot coils from coming in contact with the glass tube, since the tube is quite sure to crack after such an occurrence. The object of the platinum disk I is to maintain the coils in a proper position relative to the walls of the combustion tube, and in this way prevent contact between the coils and the glass.

The material in the boat F consists, after a combustion, of a mixture of lead peroxide, lead sulphate and—if the substance analyzed contained nitrogen—a small quantity of lead nitrate; and the amount of lead oxide, PbO —supposing all of the lead to be in that state—is known. To find the amount of sulphur, reckoned as SO_3 , it is, therefore, only necessary to reduce the peroxide and the nitrate in the mixture to oxide and weigh the residue. This reduction is effected in the following manner: The boat, F, with its contents, is placed in a hard glass tube and behind it is inserted a roll of copper wire gauze, which has been reduced by heating the gauze to red heat and then plunging it into a large test tube, in the bottom of which is a plug of

asbestos fibre that has been moistened with methyl alcohol. Both the boat and the roll are heated by lamps placed appropriately beneath the tube, and air is passed through; or the reduction is effected in a current of nitrogen flowing from a gasometer. The decomposition of the nitrate is made manifest by the appearance and subsequent disappearance of reddish vapors and the reduction of the peroxide by the disappearance of brown and red colors in the material; nevertheless, the residue, after weighing, is reheated in an atmosphere of nitrogen to ascertain if the weight remains constant.

An example will suffice to make clear the method of calculating the results of an analysis. It was found by experiment that 5 grams of the peroxide, when reduced in a current of nitrogen, yielded 4.678 grams of lead oxide, PbO . After the combustion had been finished, and the mixture reduced by heating it in an atmosphere of nitrogen, the weight of the lead oxide and lead sulphate was found to be 4.7106 grams. The weight of the SO_3 , present as lead sulphate, is, therefore, the difference between the theoretical weight of the lead oxide, PbO , and the actual weight found, which in this case amounts to 0.0326 gram, or an equivalent of 0.0130 gram of sulphur.

By way of testing the applicability of the method to compounds containing carbon, hydrogen, sulphur and oxygen, analyses were made of "sulphonal" or diethylsulphonedimethylmethane. The results obtained by the analyses are given below:

"SULPHONAL", $(\text{CH}_3)_2\text{C}(\text{SO}_2\text{C}_2\text{H}_5)_2$.			
	C.	H.	S.
Theoretical.....	36.80	7.06	28.09
Found.....	36.69	7.26	28.16
Found.....	36.47	7.12	27.90
Found.....	36.73	7.19	28.03

In the above analyses the apparatus A B C was dispensed with and the end of the Marchand tube was inserted directly in the rubber stopper at L. The time consumed in the actual combustions averaged about twenty-five minutes. Since sulphonal has a comparatively low melting-point, 126° , it was found to be of advantage to replace the current of air,

entering the combustion tube from behind, by a current of nitrogen, led in from a gasometer.

In order to extend the applicability of the method to substances containing nitrogen, carbon, hydrogen and sulphur, it is only necessary to introduce the apparatus A B C, maintained at the proper temperature, between the combustion tube and the absorption train. Analyses were made of phenylthiourea, phenylthiosemicarbazide, acetylphenylthiosemicarbazide, diphenylthiourea, parasulphaminebenzoic acid, phenylthiomethylethoxyurazole and thiourea.

The results of the analyses are given in the following table:

PHENYLTHIOUREA, $\text{NH}_2\text{CSNHC}_6\text{H}_5$.

	C.	H.	S.
Theoretical....	55.19	5.29	18.44
Found.....	55.40	5.24	18.30
Found.....	55.24	5.50	18.53

PHENYLTHIOSEMICARBAZIDE, $\text{C}_6\text{H}_5\text{NHNHCSNH}_2$.

	C.	H.	S.
Theoretical.....	50.22	5.12	19.17
Found.....	50.38	5.40	18.91
Found.....	50.39	5.50	19.30
Found.....	50.26	5.46	19.14
Found.....	50.38	5.50	19.23

ACETYPHENYLTHIOSEMICARBAZIDE, $\text{C}_6\text{H}_5(\text{CH}_3\text{CO})\text{NNHCSNH}_2$.

	C.	H.	S.
Theoretical.....	51.61	5.29	15.31
Found.....	51.83	5.30	15.41
Found.....	51.41	5.70	15.44

DIPHENYLTHIOUREA, $\text{CS}(\text{NHC}_6\text{H}_5)_2$.

	C.	H.	S.
Theoretical.....	68.35	5.29	14.05
Found.....	68.21	5.40	13.85
Found.....	68.25	5.39	13.98
Found.....	68.46	5.50	14.21
Found.....	68.43	5.43	14.09
Found.....	68.16	5.80	13.85

PARASULPHAMINEBENZOIC ACID, $C_6H_4(SO_2NH_2)COOH$.

	C.	H.	S.
Theoretical	41.76	3.50	15.93
Found	41.90	3.70	16.03
Found	41.84	3.70	16.05
Found	41.79	3.57	16.10

 PHENYLTHIOMETHYLETHOXYURAZOLE, $C_6H_5N \begin{matrix} \diagup N:C(SCH_3) \\ \diagdown C(OC_2H_5) \end{matrix} \diagup N$.
 (Melting-point 37° .)

	C.	H.	S.
Theoretical	56.15	5.56	13.67
Found	56.40	5.80	13.70
Found	56.08	5.61	13.63

THIOUREA, $CS(NH_2)_2$.

	C.	H.	S.
Theoretical	15.75	5.29	42.09
Found	15.80	5.34	42.18
Found	15.79	5.40	42.20
Found	15.84	5.39	42.30
Found	15.82	5.41	42.24

Analyses of such substances as coal, crude petroleum, dentine, etc., were also made in order to show to what degree of refinement the method is capable of being carried in technical analysis. The results obtained were perfectly satisfactory and it was determined that the applicability of the method is in no way limited to purely scientific laboratories.

In the original form of the method, as described by Morse and Taylor,¹ for the determination of carbon and hydrogen only, the oxides of nitrogen were reduced by means of metallic copper, and such a reduction, in skilled hands, is practicable and gives satisfactory results, but further experience has shown that this procedure is apt to fail when used by a beginner. In the later practice, therefore, the use of copper has been abandoned, and the oxides of nitrogen are absorbed by the peroxide of lead exactly in the same manner as described above. If carbon and hydrogen are to be determined in a compound containing nitrogen, but no sulphur, the boat of

¹ Am. Chem. Jour. **33**, 591.

peroxide at F may be dispensed with, and the contents of A, maintained at the proper temperature, may be relied upon to absorb all of the oxides of nitrogen. It is well, however, in the burning of substances which do not contain sulphur, to replace the plugs of asbestos J and J' by oxidized rolls of copper wire gauze, which are heated, during the combustion, by broad flames placed beneath the tube.

The determination of the halogens, simultaneously with carbon and hydrogen, has not been attempted in this investigation, but the indications point very clearly to the conclusion that at least chlorine and bromine could be absorbed in precisely the same manner as the oxides of sulphur. Further work upon the problem of the absorption of the halogens, by the use of the electrical method, will be carried out in the near future.

BIOGRAPHICAL.

C. Walter Gray was born at Chrisman, Edgar County, Illinois, June 24, 1882.

He prepared for college at the Chrisman High School. In the fall of 1899 he entered the Illinois Wesleyan University, graduating in 1903 with the degree of Bachelor of Science.

In October 1903, he entered the Johns Hopkins University as a student of chemistry.

His subordinate subjects have been Physical Chemistry and Mineralogy.

